

MOLECULAR PROCESSES IN COMETS

NAGW-1561

Annual Progress Report No. 2

For the period 1 November 1992 to 31 October 1993

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August 1993

Prepared for
National Aeronautics and Space Administration
Washington, D. C. 20546

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The Smithsonian Astrophysical Observatory
is a member of the
Harvard-Smithsonian Center for Astrophysics

The NASA Technical Officer for this grant is Dr. Jay Bergstralh, Code SL,
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N94-15189

Unclas

G3/90 0185665

(NASA-CR-194148) MOLECULAR
PROCESSES IN COMETS Annual Progress
Report No. 2, 1 Nov. 1992 - 31 Oct.
1993 (Smithsonian Astrophysical
Observatory) 38 p

the exchange transitions which occur at small internuclear distances, the rate coefficients for the three surfaces agree quite well. For the direct transitions, there are significant differences for the pure rotational transitions from $j=0$ to 2 and from $j=1$ to $j=3$ in which there is no change in vibration. For higher j the differences tend to disappear, suggesting that the rotational angular momentum can couple to the orbital angular momentum to overcome the centrifugal barrier so that the excitation is driven by a torque operating at small separations of H and H₂ where the three potential energy surfaces are similar.

There are of course substantial questions as to the validity of semi-classical calculations. We have also performed complete numerically exact quantum mechanical calculations for the processes in which vJ changes from 00 to 01, 02 and 03 and from 01 to 00, 02 and 03. The calculations are computationally intensive and have been carried out only for the DMBE surface and for temperatures up to 1000K. Table 2 is a comparison of semi-classical and quantum calculations for the rate coefficients of the $(0,0) \rightarrow (0,2)$ and $(0,1) \rightarrow (0,3)$ transitions in cm^3s^{-1} . It appears that the semi-classical calculations are useful, indeed accurate, down

to temperatures of about twice the threshold temperature of the reaction which is 509K for $(0,0) \rightarrow (0,2)$ and 944K for $(0,1) \rightarrow (0,3)$.

A first draft of a paper on the quantal calculations has been written and is attached.

We have been studying the problem of the photodissociation of NH. Our preliminary study has identified the mechanisms and has definitely established that the lifetime is of the order of 10^5 s but it also demonstrates that a more detailed analysis is needed. Dr. M. A'Hearn has provided us with his data on the fluorescent population of the NH rotational and fine-structure levels from which we should be able to predict accurate photodissociation lifetimes.

We have also under study an investigation of the distribution rate of C_2 but have not so far identified the mechanism responsible. For CO, we are carrying out explicit calculations. The literature value is based on inadequate laboratory data.

A review of H_3^+ in terrestrial and extraterrestrial environments was prepared for a volume of Advances in Atomic, Molecular and Optical Physics in honor of Sir David Bates. A copy is attached.

References

- A. I. Boothroyd, W. J. Keogh, P. G. Martin and M. J. Peterson, 1991, J. Chem. Phys. 95, 4343.
- M. E. Mandy and P. G. Martin, 1993, ApJS 86, 199.
- A. J. C. Varandas, F. B. Brown, C. A. Mead, D. G. Truhlar and N. G. Blais, 1987, J. Chem. Phys. 86, 6258.

Table 1a. State to state rate coefficients for H+H₂ at 1000K with the LSTH potential.

(v,j) from	to	(0,0)	(0,1)	0,2	(0,3)	(0,4)	(0,5)	(0,6)	(0,7)	(0,8)	(0,9)	(1,0)	(1,1)	(1,2)	(1,3)	(1,4)	(1,5)
(0,0)	——	0.0(+00)	9.0(-12)	0.0(+00)	6.0(-13)	0.0(+00)	2.3(-14)	0.0(+00)	7.2(-15)	0.0(+00)	2.9(-15)	0.0(+00)	5.2(-15)	0.0(+00)	3.3(-16)	0.0(+00)	
	1.1(-13)	6.8(-13)	1.7(-13)	4.6(-13)	3.7(-14)	2.8(-14)	1.7(-14)	7.7(-15)	1.4(-15)	9.9(-16)	5.0(-16)	2.3(-15)	1.1(-15)	3.0(-15)	2.4(-16)	5.8(-16)	
(0,1)	0.0(+00)	——	0.0(+00)	3.0(-12)	0.0(+00)	2.2(-13)	0.0(+00)	1.4(-14)	0.0(+00)	6.9(-16)	0.0(+00)	1.7(-15)	0.0(+00)	7.9(-16)	0.0(+00)	6.1(-17)	
	8.9(-14)	7.0(-13)	1.3(-13)	4.1(-13)	2.9(-14)	1.6(-13)	1.2(-14)	1.4(-14)	1.1(-15)	1.2(-15)	6.2(-16)	2.9(-15)	1.2(-15)	2.5(-15)	2.6(-16)	4.1(-16)	
(0,2)	3.0(-12)	0.0(+00)	——	0.0(+00)	1.5(-12)	0.0(+00)	7.3(-14)	0.0(+00)	5.4(-15)	0.0(+00)	1.3(-15)	0.0(+00)	2.7(-15)	0.0(+00)	4.3(-16)	0.0(+00)	
	5.6(-14)	3.4(-13)	7.5(-14)	3.8(-13)	3.1(-14)	2.2(-13)	1.0(-14)	1.7(-14)	1.5(-15)	1.6(-15)	6.4(-16)	5.8(-15)	1.4(-15)	2.4(-15)	4.1(-16)	3.1(-16)	
(0,3)	0.0(+00)	3.0(-12)	0.0(+00)	——	0.0(+00)	1.0(-12)	0.0(+00)	2.0(-14)	0.0(+00)	1.2(-15)	0.0(+00)	2.4(-15)	0.0(+00)	1.2(-15)	0.0(+00)	7.9(-16)	
	6.0(-14)	4.1(-13)	1.5(-13)	5.0(-13)	1.1(-13)	1.5(-13)	1.8(-14)	3.0(-14)	3.0(-15)	3.4(-15)	5.9(-16)	7.2(-15)	1.8(-15)	3.1(-15)	4.8(-16)	2.7(-16)	
(0,4)	3.6(-13)	0.0(+00)	2.7(-12)	0.0(+00)	——	0.0(+00)	7.0(-13)	0.0(+00)	2.1(-14)	0.0(+00)	1.7(-15)	0.0(+00)	2.6(-15)	0.0(+00)	9.7(-16)	0.0(+00)	
	2.2(-14)	1.3(-13)	5.6(-14)	5.0(-13)	1.7(-13)	1.2(-13)	2.7(-14)	4.3(-14)	5.4(-15)	6.1(-15)	8.5(-16)	5.8(-15)	2.2(-15)	4.5(-15)	6.8(-16)	8.3(-16)	
(0,5)	0.0(+00)	6.2(-13)	0.0(+00)	2.8(-12)	0.0(+00)	——	0.0(+00)	4.4(-13)	0.0(+00)	5.4(-15)	0.0(+00)	2.7(-15)	0.0(+00)	2.8(-15)	0.0(+00)	1.4(-15)	
	1.0(-14)	4.4(-13)	2.5(-13)	4.4(-13)	7.3(-14)	3.7(-13)	4.1(-14)	7.7(-14)	1.1(-14)	9.5(-15)	1.0(-15)	5.1(-15)	2.3(-15)	7.5(-15)	1.4(-15)	1.8(-15)	
(0,6)	5.7(-14)	0.0(+00)	5.4(-13)	0.0(+00)	2.9(-12)	0.0(+00)	——	0.0(+00)	3.7(-13)	0.0(+00)	7.1(-16)	0.0(+00)	3.7(-15)	0.0(+00)	4.9(-15)	0.0(+00)	
	4.3(-14)	2.3(-13)	7.8(-14)	3.4(-13)	1.1(-13)	2.8(-13)	7.8(-14)	1.6(-13)	2.7(-14)	1.5(-14)	1.1(-15)	1.0(-14)	4.6(-15)	1.3(-14)	3.0(-15)	3.2(-15)	
(0,7)	0.0(+00)	2.3(-13)	0.0(+00)	3.3(-13)	0.0(+00)	2.6(-12)	0.0(+00)	——	0.0(+00)	2.6(-13)	0.0(+00)	4.0(-15)	0.0(+00)	2.0(-14)	0.0(+00)	9.1(-15)	
	1.7(-14)	2.3(-13)	1.1(-13)	5.0(-13)	1.6(-13)	4.5(-13)	1.4(-13)	1.3(-13)	4.1(-14)	3.2(-14)	3.7(-15)	2.1(-14)	9.7(-15)	2.2(-14)	8.0(-15)	7.6(-15)	
(0,8)	1.4(-13)	0.0(+00)	3.2(-13)	0.0(+00)	7.2(-13)	0.0(+00)	3.0(-12)	0.0(+00)	——	0.0(+00)	0.0(+00)	0.0(+00)	1.5(-14)	0.0(+00)	6.5(-15)	0.0(+00)	
	2.7(-14)	1.6(-13)	9.0(-14)	4.6(-13)	1.8(-13)	5.9(-13)	2.2(-13)	3.8(-13)	4.5(-14)	8.6(-14)	1.0(-14)	1.8(-14)	1.5(-14)	3.8(-14)	1.6(-14)	2.3(-14)	
(0,9)	0.0(+00)	1.2(-13)	0.0(+00)	2.2(-13)	0.0(+00)	3.4(-13)	0.0(+00)	2.8(-12)	0.0(+00)	——	0.0(+00)	0.0(+00)	0.0(+00)	0.0(+00)	0.0(+00)	6.5(-14)	
	2.3(-14)	2.1(-13)	1.2(-13)	6.0(-13)	2.4(-13)	6.0(-13)	1.4(-13)	3.5(-13)	1.0(-13)	1.9(-13)	4.6(-14)	1.4(-13)	4.6(-14)	2.1(-13)	1.7(-14)	6.5(-14)	
(1,0)	1.1(-12)	0.0(+00)	1.6(-12)	0.0(+00)	1.1(-12)	0.0(+00)	1.1(-13)	0.0(+00)	0.0(+00)	0.0(+00)	0.0(+00)	——	0.0(+00)	5.6(-11)	0.0(+00)	0.0(+00)	
	2.0(-13)	1.9(-12)	7.7(-13)	1.8(-12)	5.7(-13)	1.1(-12)	1.7(-13)	6.8(-13)	2.0(-13)	7.9(-13)	9.7(-13)	4.9(-12)	9.6(-13)	1.8(-12)	2.9(-13)	5.6(-13)	
(1,1)	0.0(+00)	6.7(-13)	0.0(+00)	9.6(-13)	0.0(+00)	3.8(-13)	0.0(+00)	9.6(-14)	0.0(+00)	0.0(+00)	0.0(+00)	——	0.0(+00)	1.6(-11)	0.0(+00)	1.1(-12)	
	1.2(-13)	1.1(-12)	9.1(-13)	2.9(-12)	5.0(-13)	7.2(-13)	2.2(-13)	5.0(-13)	4.8(-14)	3.1(-13)	6.5(-13)	3.9(-12)	1.0(-12)	1.5(-12)	2.9(-13)	5.3(-13)	
(1,2)	6.7(-13)	0.0(+00)	1.1(-12)	0.0(+00)	5.7(-13)	0.0(+00)	1.9(-13)	0.0(+00)	9.6(-14)	0.0(+00)	1.8(-11)	0.0(+00)	——	0.0(+00)	7.4(-12)	0.0(+00)	
	1.4(-13)	1.2(-12)	5.5(-13)	1.8(-12)	4.8(-13)	7.9(-13)	2.4(-13)	5.7(-13)	9.6(-14)	2.6(-13)	3.1(-13)	2.5(-12)	9.6(-13)	1.6(-12)	4.4(-13)	5.0(-13)	
(1,3)	0.0(+00)	3.0(-13)	0.0(+00)	4.5(-13)	0.0(+00)	3.8(-13)	0.0(+00)	4.5(-13)	0.0(+00)	6.6(-14)	0.0(+00)	1.5(-11)	0.0(+00)	——	0.0(+00)	4.8(-12)	
	1.5(-13)	9.6(-13)	3.6(-13)	1.2(-12)	3.8(-13)	1.0(-12)	2.6(-13)	5.1(-13)	9.4(-14)	4.4(-13)	2.3(-13)	1.5(-12)	6.2(-13)	2.4(-12)	6.7(-13)	5.9(-13)	
(1,4)	7.1(-14)	0.0(+00)	2.9(-13)	0.0(+00)	3.6(-13)	0.0(+00)	4.3(-13)	0.0(+00)	7.1(-14)	0.0(+00)	1.8(-12)	0.0(+00)	1.2(-11)	0.0(+00)	——	0.0(+00)	
	5.3(-14)	4.3(-13)	2.7(-13)	8.0(-13)	2.5(-13)	8.0(-13)	2.7(-13)	8.0(-13)	1.8(-13)	1.6(-13)	1.6(-13)	1.2(-12)	7.5(-13)	2.9(-12)	7.8(-13)	1.1(-12)	
(1,5)	0.0(+00)	6.0(-14)	0.0(+00)	7.9(-13)	0.0(+00)	4.8(-13)	0.0(+00)	5.4(-13)	0.0(+00)	3.6(-13)	0.0(+00)	2.7(-12)	0.0(+00)	1.2(-11)	0.0(+00)	——	
	7.6(-14)	4.1(-13)	1.2(-13)	2.7(-13)	1.8(-13)	6.4(-13)	1.7(-13)	4.5(-13)	1.5(-13)	3.6(-13)	1.8(-13)	1.3(-12)	5.0(-13)	1.5(-12)	6.4(-13)	1.6(-12)	

Table 1b. State to state rate coefficients for H+H₂ at 1000K with the BKMP potential.

(v,j) from	to (0,0)	(0,1)	0,2	(0,3)	(0,4)	(0,5)	(0,6)	(0,7)	(0,8)	(0,9)	(1,0)	(1,1)	(1,2)	(1,3)	(1,4)	(1,5)
(0,0)	——	0.0(+00)	1.6(-11)	0.0(+00)	7.4(-13)	0.0(+00)	8.0(-14)	0.0(+00)	0.0(+00)	0.0(+00)	2.0(-15)	0.0(+00)	1.5(-15)	0.0(+00)	3.3(-16)	0.0(+00)
	1.3(-13)	5.4(-13)	2.8(-13)	6.9(-13)	5.6(-14)	1.7(-13)	1.7(-14)	2.3(-14)	1.8(-15)	3.3(-16)	8.6(-16)	5.0(-15)	9.2(-16)	3.0(-15)	3.3(-16)	3.5(-16)
(0,1)	0.0(+00)	——	0.0(+00)	3.8(-12)	0.0(+00)	1.5(-13)	0.0(+00)	1.8(-14)	0.0(+00)	8.7(-16)	0.0(+00)	2.4(-15)	0.0(+00)	1.2(-15)	0.0(+00)	1.2(-16)
	7.1(-14)	5.3(-13)	2.5(-13)	4.1(-13)	6.6(-14)	1.4(-13)	2.0(-14)	2.3(-14)	1.8(-15)	6.5(-16)	7.3(-16)	4.2(-15)	9.5(-16)	2.4(-15)	3.5(-16)	4.6(-16)
(0,2)	5.3(-12)	0.0(+00)	——	0.0(+00)	2.6(-12)	0.0(+00)	8.4(-14)	0.0(+00)	4.2(-15)	0.0(+00)	1.4(-15)	0.0(+00)	3.4(-15)	0.0(+00)	9.8(-16)	0.0(+00)
	9.4(-14)	6.2(-13)	2.6(-13)	4.6(-13)	1.1(-13)	1.5(-13)	2.5(-14)	2.3(-14)	3.4(-15)	7.1(-16)	5.3(-15)	5.3(-15)	1.3(-15)	1.9(-15)	5.2(-16)	4.6(-16)
(0,3)	0.0(+00)	3.8(-12)	0.0(+00)	——	0.0(+00)	1.5(-12)	0.0(+00)	3.4(-14)	0.0(+00)	1.9(-15)	0.0(+00)	4.3(-15)	0.0(+00)	1.4(-15)	0.0(+00)	4.3(-16)
	9.1(-14)	4.1(-13)	1.8(-13)	7.3(-13)	1.5(-13)	2.0(-13)	2.7(-14)	2.9(-14)	4.4(-15)	3.4(-15)	7.9(-16)	6.0(-15)	2.0(-15)	3.1(-15)	7.7(-16)	5.0(-16)
(0,4)	4.4(-13)	0.0(+00)	4.7(-12)	0.0(+00)	——	0.0(+00)	7.0(-13)	0.0(+00)	1.8(-14)	0.0(+00)	8.5(-16)	0.0(+00)	2.6(-15)	0.0(+00)	9.7(-16)	0.0(+00)
	3.3(-14)	3.0(-13)	1.9(-13)	7.0(-13)	1.8(-13)	3.5(-13)	3.9(-14)	5.0(-14)	3.8(-15)	6.7(-15)	8.5(-16)	6.8(-15)	2.3(-15)	5.0(-15)	6.8(-16)	1.0(-15)
(0,5)	0.0(+00)	4.2(-13)	0.0(+00)	4.2(-12)	0.0(+00)	——	0.0(+00)	5.4(-13)	0.0(+00)	9.8(-15)	0.0(+00)	2.7(-15)	0.0(+00)	2.6(-15)	0.0(+00)	5.2(-16)
	6.2(-14)	4.0(-13)	1.7(-13)	5.6(-13)	2.2(-13)	4.7(-13)	8.0(-14)	8.5(-14)	6.5(-15)	1.1(-14)	8.7(-16)	8.2(-15)	2.3(-15)	9.2(-15)	7.2(-16)	2.1(-15)
(0,6)	2.0(-13)	0.0(+00)	6.3(-13)	0.0(+00)	2.9(-12)	0.0(+00)	——	0.0(+00)	3.3(-13)	0.0(+00)	0.0(+00)	0.0(+00)	5.5(-15)	0.0(+00)	2.4(-15)	0.0(+00)
	4.3(-14)	3.8(-13)	1.8(-13)	5.1(-13)	1.6(-13)	5.3(-13)	1.1(-13)	8.6(-14)	1.9(-14)	1.7(-14)	1.4(-15)	1.0(-14)	5.0(-15)	2.1(-14)	2.2(-15)	5.2(-15)
(0,7)	0.0(+00)	3.0(-13)	0.0(+00)	5.7(-13)	0.0(+00)	3.2(-12)	0.0(+00)	——	0.0(+00)	2.6(-13)	0.0(+00)	1.2(-14)	0.0(+00)	1.6(-14)	0.0(+00)	6.1(-15)
	5.0(-14)	3.8(-13)	1.5(-13)	4.8(-13)	1.8(-13)	5.0(-13)	7.5(-14)	1.3(-13)	3.5(-14)	3.2(-14)	4.2(-15)	2.1(-14)	1.1(-14)	2.2(-14)	6.9(-15)	9.1(-15)
(0,8)	0.0(+00)	0.0(+00)	2.5(-13)	0.0(+00)	6.1(-13)	0.0(+00)	2.6(-12)	0.0(+00)	——	0.0(+00)	1.1(-14)	0.0(+00)	3.0(-14)	0.0(+00)	2.0(-14)	0.0(+00)
	3.6(-14)	2.7(-13)	2.1(-13)	6.7(-13)	1.3(-13)	3.5(-13)	1.5(-13)	3.2(-13)	5.4(-14)	9.9(-14)	1.1(-14)	2.8(-14)	1.5(-14)	6.0(-14)	2.1(-14)	1.9(-14)
(0,9)	0.0(+00)	1.5(-13)	0.0(+00)	3.4(-13)	0.0(+00)	6.2(-13)	0.0(+00)	2.8(-12)	0.0(+00)	——	0.0(+00)	0.0(+00)	5.8(-11)	0.0(+00)	3.0(-12)	0.0(+00)
	7.7(-15)	1.2(-13)	1.1(-13)	6.0(-13)	2.6(-13)	7.2(-13)	1.6(-13)	3.5(-13)	1.2(-13)	3.2(-13)	7.7(-15)	9.3(-14)	5.4(-14)	2.3(-13)	1.7(-14)	7.6(-14)
(1,0)	8.0(-13)	0.0(+00)	1.7(-12)	0.0(+00)	5.7(-13)	0.0(+00)	0.0(+00)	0.0(+00)	2.3(-13)	0.0(+00)	——	0.0(+00)	1.0(-12)	1.1(-12)	4.2(-13)	6.5(-13)
	3.4(-13)	2.2(-12)	8.5(-13)	2.4(-12)	5.7(-13)	9.4(-13)	2.3(-13)	7.7(-13)	2.3(-13)	1.3(-13)	9.4(-13)	3.3(-12)	1.0(-12)	1.1(-12)	4.2(-13)	6.5(-13)
(1,1)	0.0(+00)	9.6(-13)	0.0(+00)	1.7(-12)	0.0(+00)	3.8(-13)	0.0(+00)	2.9(-13)	0.0(+00)	0.0(+00)	0.0(+00)	——	0.0(+00)	2.0(-11)	0.0(+00)	1.4(-12)
	2.6(-13)	1.6(-12)	8.4(-13)	2.4(-12)	6.0(-13)	1.1(-12)	2.2(-13)	5.0(-13)	7.2(-14)	2.1(-13)	4.3(-13)	3.4(-12)	1.3(-12)	1.8(-12)	3.9(-13)	5.1(-13)
(1,2)	1.9(-13)	0.0(+00)	1.3(-12)	0.0(+00)	5.7(-13)	0.0(+00)	2.9(-13)	0.0(+00)	1.9(-13)	0.0(+00)	1.9(-11)	0.0(+00)	——	0.0(+00)	9.6(-12)	0.0(+00)
	1.2(-13)	9.3(-13)	5.0(-13)	2.0(-12)	5.0(-13)	7.9(-13)	2.6(-13)	6.5(-13)	9.6(-14)	3.0(-13)	3.3(-13)	3.3(-12)	1.6(-12)	2.3(-12)	4.7(-13)	4.7(-13)
(1,3)	0.0(+00)	4.5(-13)	0.0(+00)	5.3(-13)	0.0(+00)	1.5(-13)	0.0(+00)	3.8(-13)	0.0(+00)	6.6(-14)	0.0(+00)	1.9(-11)	0.0(+00)	——	0.0(+00)	5.9(-12)
	1.5(-13)	9.0(-13)	2.8(-13)	1.2(-12)	4.1(-13)	1.2(-12)	4.1(-13)	5.1(-13)	1.5(-13)	4.9(-13)	1.3(-13)	1.7(-12)	9.0(-13)	2.9(-12)	7.5(-13)	8.0(-13)
(1,4)	7.1(-14)	0.0(+00)	6.4(-13)	0.0(+00)	0.0(+00)	0.0(+00)	2.1(-13)	0.0(+00)	0.0(+00)	0.0(+00)	1.6(-12)	0.0(+00)	1.6(-11)	0.0(+00)	——	0.0(+00)
	7.1(-14)	5.9(-13)	3.4(-13)	1.3(-12)	2.5(-13)	4.3(-13)	2.0(-13)	7.0(-13)	2.3(-13)	1.6(-13)	2.3(-13)	1.7(-12)	8.0(-13)	3.3(-12)	1.1(-12)	1.3(-12)
(1,5)	0.0(+00)	1.2(-13)	0.0(+00)	4.2(-13)	0.0(+00)	1.8(-13)	0.0(+00)	3.6(-13)	0.0(+00)	4.2(-13)	0.0(+00)	3.5(-12)	0.0(+00)	1.5(-11)	0.0(+00)	——
	4.5(-14)	4.5(-13)	1.8(-13)	5.0(-13)	2.3(-13)	7.3(-13)	2.7(-13)	5.4(-13)	1.2(-13)	4.1(-13)	2.1(-13)	1.3(-12)	4.7(-13)	2.1(-12)	8.0(-13)	2.1(-12)

Table 1c. State to state rate coefficients for H+H₂ at 1000K with the DMBE potential.

(v _j) from	to	(0,0)	(0,1)	0,2	(0,3)	(0,4)	(0,5)	(0,6)	(0,7)	(0,8)	(0,9)	(1,0)	(1,1)	(1,2)	(1,3)	(1,4)	(1,5)
(0,0)	——	0.0(+00)	8.4(-11)	0.0(+00)	4.5(-13)	0.0(+00)	3.4(-14)	0.0(+00)	5.4(-15)	0.0(+00)	2.9(-15)	0.0(+00)	2.2(-15)	0.0(+00)	6.5(-16)	0.0(+00)	
	2.0(-13)	6.8(-13)	2.3(-13)	8.1(-13)	7.4(-14)	0.0(+00)	2.0(-14)	1.5(-14)	1.4(-15)	3.3(-16)	5.0(-16)	1.8(-15)	7.4(-16)	7.5(-16)	3.3(-16)	3.5(-16)	
(0,1)	0.0(+00)	——	0.0(+00)	8.2(-12)	0.0(+00)	3.0(-13)	0.0(+00)	8.1(-15)	0.0(+00)	5.2(-16)	0.0(+00)	2.7(-15)	0.0(+00)	7.9(-16)	0.0(+00)	1.2(-16)	
	8.9(-14)	5.3(-13)	2.0(-13)	4.1(-13)	6.6(-14)	6.6(-14)	1.4(-14)	1.8(-14)	2.1(-15)	3.9(-16)	6.2(-16)	4.4(-15)	1.0(-15)	1.5(-15)	2.6(-16)	4.6(-16)	
(0,2)	2.8(-11)	0.0(+00)	——	0.0(+00)	1.9(-12)	0.0(+00)	7.6(-14)	0.0(+00)	3.6(-15)	0.0(+00)	1.3(-15)	0.0(+00)	2.5(-15)	0.0(+00)	8.7(-16)	0.0(+00)	
	7.5(-14)	5.1(-13)	2.6(-13)	4.2(-13)	8.7(-14)	1.2(-13)	1.3(-14)	1.5(-14)	2.1(-15)	1.4(-15)	6.6(-16)	5.8(-15)	1.7(-15)	2.3(-15)	3.3(-16)	3.5(-16)	
(0,3)	0.0(+00)	8.2(-12)	0.0(+00)	——	0.0(+00)	5.9(-13)	0.0(+00)	2.2(-14)	0.0(+00)	1.2(-15)	0.0(+00)	2.2(-15)	0.0(+00)	1.2(-15)	0.0(+00)	4.3(-16)	
	1.1(-13)	4.1(-13)	1.7(-13)	5.4(-13)	9.5(-14)	1.5(-13)	2.5(-14)	1.7(-14)	2.8(-15)	3.4(-15)	6.5(-16)	6.0(-15)	2.1(-15)	3.0(-15)	4.2(-16)	2.3(-16)	
(0,4)	2.7(-13)	0.0(+00)	3.4(-12)	0.0(+00)	——	0.0(+00)	3.3(-13)	0.0(+00)	7.5(-15)	0.0(+00)	8.5(-16)	0.0(+00)	1.8(-15)	0.0(+00)	1.2(-15)	0.0(+00)	
	4.4(-14)	3.0(-13)	1.6(-13)	4.3(-13)	1.3(-13)	2.3(-13)	4.1(-14)	4.6(-14)	4.0(-15)	5.5(-15)	8.5(-16)	6.3(-15)	2.1(-15)	3.8(-15)	4.9(-16)	6.9(-16)	
(0,5)	0.0(+00)	8.3(-13)	0.0(+00)	1.7(-12)	0.0(+00)	——	0.0(+00)	2.6(-13)	0.0(+00)	4.9(-15)	0.0(+00)	3.4(-15)	0.0(+00)	0.0(+00)	0.0(+00)	8.6(-16)	
	0.0(+00)	1.9(-13)	1.3(-13)	4.4(-13)	1.5(-13)	4.4(-13)	6.0(-14)	7.7(-14)	6.5(-15)	9.5(-15)	1.0(-15)	5.6(-15)	1.8(-15)	5.0(-15)	7.2(-16)	1.4(-15)	
(0,6)	8.5(-14)	0.0(+00)	5.7(-13)	0.0(+00)	1.4(-12)	0.0(+00)	——	0.0(+00)	1.5(-13)	0.0(+00)	1.4(-15)	0.0(+00)	7.3(-15)	0.0(+00)	5.7(-15)	0.0(+00)	
	5.0(-14)	2.6(-13)	1.0(-13)	4.7(-13)	1.7(-13)	4.1(-13)	8.5(-14)	6.7(-14)	1.8(-14)	1.8(-14)	8.8(-16)	1.0(-14)	3.7(-15)	1.3(-14)	3.0(-15)	2.0(-15)	
(0,7)	0.0(+00)	1.3(-13)	0.0(+00)	3.7(-13)	0.0(+00)	1.5(-12)	0.0(+00)	——	0.0(+00)	2.0(-13)	0.0(+00)	4.0(-15)	0.0(+00)	2.3(-14)	0.0(+00)	1.0(-14)	
	3.3(-14)	3.0(-13)	1.0(-13)	2.8(-13)	1.7(-13)	4.5(-13)	5.8(-14)	1.3(-13)	4.1(-14)	2.6(-14)	3.3(-15)	1.5(-14)	7.2(-15)	2.0(-14)	4.3(-15)	4.6(-15)	
(0,8)	1.1(-13)	0.0(+00)	2.2(-13)	0.0(+00)	2.5(-13)	0.0(+00)	1.2(-12)	0.0(+00)	——	0.0(+00)	0.0(+00)	0.0(+00)	0.0(+00)	0.0(+00)	1.3(-14)	0.0(+00)	
	2.7(-14)	3.2(-13)	1.3(-13)	4.3(-13)	1.3(-13)	3.5(-13)	1.4(-13)	3.8(-13)	9.9(-14)	9.9(-14)	8.6(-15)	1.8(-14)	1.8(-14)	2.3(-14)	9.8(-15)	9.3(-15)	
(0,9)	0.0(+00)	9.3(-14)	0.0(+00)	2.2(-13)	0.0(+00)	3.1(-13)	0.0(+00)	2.1(-12)	0.0(+00)	——	0.0(+00)	0.0(+00)	0.0(+00)	0.0(+00)	0.0(+00)	2.2(-14)	
	7.7(-15)	6.9(-14)	1.0(-13)	6.0(-13)	2.2(-13)	6.0(-13)	1.7(-13)	2.8(-13)	1.2(-13)	3.2(-13)	7.7(-15)	1.2(-13)	5.4(-14)	1.9(-13)	5.7(-15)	4.1(-14)	
(1,0)	1.1(-12)	0.0(+00)	1.6(-12)	0.0(+00)	5.7(-13)	0.0(+00)	2.3(-13)	0.0(+00)	0.0(+00)	0.0(+00)	——	0.0(+00)	2.0(-10)	0.0(+00)	2.9(-12)	0.0(+00)	
	2.0(-13)	1.9(-12)	8.0(-13)	2.0(-12)	5.7(-13)	1.1(-12)	1.4(-13)	6.0(-13)	1.7(-13)	1.3(-13)	1.3(-12)	5.9(-12)	5.9(-13)	2.0(-12)	1.6(-13)	4.2(-13)	
(1,1)	0.0(+00)	1.1(-12)	0.0(+00)	8.6(-13)	0.0(+00)	4.8(-13)	0.0(+00)	9.6(-14)	0.0(+00)	0.0(+00)	0.0(+00)	——	0.0(+00)	3.4(-11)	0.0(+00)	8.0(-13)	
	9.6(-14)	1.7(-12)	9.1(-13)	2.4(-12)	5.5(-13)	7.9(-13)	2.2(-13)	3.6(-13)	4.8(-14)	2.6(-13)	7.6(-13)	4.0(-12)	9.2(-13)	1.7(-12)	2.8(-13)	3.6(-13)	
(1,2)	2.9(-13)	0.0(+00)	9.6(-13)	0.0(+00)	3.8(-13)	0.0(+00)	3.8(-13)	0.0(+00)	0.0(+00)	0.0(+00)	6.5(-11)	0.0(+00)	——	0.0(+00)	9.0(-12)	0.0(+00)	
	9.6(-14)	1.0(-12)	6.5(-13)	2.1(-12)	4.5(-13)	6.5(-13)	1.9(-13)	4.3(-13)	1.2(-13)	3.0(-13)	1.9(-13)	2.3(-12)	1.1(-12)	1.7(-12)	3.1(-13)	4.4(-13)	
(1,3)	0.0(+00)	3.0(-13)	0.0(+00)	4.5(-13)	0.0(+00)	0.0(+00)	0.0(+00)	5.3(-13)	0.0(+00)	6.6(-14)	0.0(+00)	3.3(-11)	0.0(+00)	——	0.0(+00)	3.7(-12)	
	3.8(-14)	5.6(-13)	3.4(-13)	1.1(-12)	3.2(-13)	6.8(-13)	2.6(-13)	4.5(-13)	5.6(-14)	3.9(-13)	2.4(-13)	1.6(-12)	6.4(-13)	1.9(-12)	4.9(-13)	7.3(-13)	
(1,4)	1.4(-13)	0.0(+00)	5.7(-13)	0.0(+00)	4.3(-13)	0.0(+00)	5.0(-13)	0.0(+00)	1.4(-13)	0.0(+00)	1.6(-12)	0.0(+00)	1.5(-11)	0.0(+00)	——	0.0(+00)	
	7.1(-14)	4.3(-13)	2.1(-13)	7.0(-13)	1.8(-13)	4.3(-13)	2.7(-13)	4.3(-13)	1.1(-13)	5.3(-14)	8.9(-14)	1.2(-12)	5.2(-13)	2.1(-12)	7.3(-13)	8.9(-13)	
(1,5)	0.0(+00)	1.2(-13)	0.0(+00)	4.2(-13)	0.0(+00)	3.0(-13)	0.0(+00)	6.0(-13)	0.0(+00)	1.2(-13)	0.0(+00)	2.0(-12)	0.0(+00)	4.4(-13)	0.0(+00)	——	
	4.5(-14)	4.5(-13)	1.4(-13)	2.3(-13)	1.5(-13)	5.0(-13)	1.1(-13)	2.7(-13)	6.0(-14)	2.3(-13)	1.4(-13)	9.1(-13)	4.4(-13)	1.9(-12)	5.3(-13)	1.1(-12)	

Table 2. State to state rate coefficients for $\text{H}+\text{H}_2$
with the DMBE potential

temperature	(0,0) to (0,2)		(0,1) to (0,3)	
	This paper	Sun and Dalgarno	This paper	Sun and Dalgarno
200	2.0(-13)	1.9(-12)	1.7(-16)	1.1(-13)
400	7.1(-12)	1.5(-11)	9.6(-14)	2.1(-12)
600	2.3(-11)	3.4(-11)	9.5(-13)	6.7(-12)
800	5.4(-11)	5.4(-11)	4.0(-12)	1.3(-11)
1000	7.6(-11)	7.3(-11)	7.8(-12)	2.0(-11)

PRELIMINARY DRAFT

Rotational excitation of H_2 in collision with H

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July, 1993

Abstract

The rate coefficients for the excitation from the $j = 0$ to the $j = 2$ rotational level of H_2 and from the $j = 1$ to the $j = 3$ rotational level by impacts with hydrogen atoms are calculated for temperatures between 30K and 1000K using a fully-converged complete close-coupling method. Rate coefficients are also obtained for the reactive process of ortho-para conversion where j is excited from $j = 0$ to $j = 1, 3$ and from $j = 1$ to $j = 2$. The interference between the direct and reactive channels is taken into account as is the geometric phase resulting from the adiabatic separation of electronic and nuclear motion that generates the potential energy surface. Convenient analytical representations of the rate coefficients are presented.

1 Introduction

The distribution of molecular hydrogen between its ortho and para forms is an important aspect of the physics and chemistry of the atmosphere of the Jovian planets (Massie and Hunten 1982, Conrath and Gierasch 1984), and of interstellar molecular clouds (Dalgarno, Black and Weisheit 1973, Spitzer, Cochran and Hirshfeld 1974, Jura 1975, Black and Dalgarno 1977, Takayanagi, Sakimoto and Onda 1987, Pineau des Forêts, Flower and McCarroll 1991, Abgrall et al. 1992). Depending on the physical environments, conversions between ortho and para forms may be effected by reactive collisions between H and H₂ in which the rotational quantum number j changes by an odd number. Rotational excitations in which j changes by an even number in non-reactive and reactive collisions of H with H₂ are important to the distribution of the relative populations of the rotational levels of H₂ and to the cooling efficiency of hydrogen rich gas.

Because of its fundamental significance to the theory of chemical reactions, the reactive scattering of H by H₂ has received considerable attention and powerful methods have been developed for and applied to the calculation of the cross sections (Schatz and Kuppermann 1976, Mladenovic et al. 1988, Zhang and Miller 1988, 1989, Park and Light 1989, Walker and Light 1989, Manolopoulos and Wyatt 1989, 1990, Launay and Dourneuf 1989, Miller and Zhang 1991). Most of the effort has been devoted to an exploration of the dynamical resonances that may or may not have been detected experimen-

tally at energies near 1eV (Nieh and Valentini 1988, 1990, Klinner, Adelman and Zare 1991), but some calculations of reactive scattering at lower temperatures have been carried out (Park and Light 1989, Takayanagi and Masaki 1991) and Mandy and Martin (1991, 1992, 1993) have used a semi-classical procedure to calculate rate coefficients for all the possible reactive and non-reactive rovibrational transitions in H_2 for temperatures down to 600K.

No calculations of rotational transitions at lower temperatures have been reported since the calculations of Green and Truhlar (1979) who did close-coupling calculations of non-reactive rotational excitation processes within the rigid rotor approximation, neglecting any interference between reactive and non-reactive channels. They obtained rate coefficients considerably smaller than the results of earlier close-coupling calculations of Allison and Dalgarno (1967), Wolken, Miller and Karplus (1972), Chu and Dalgarno (1975), and McGuire and Kruger (1975).

In many astrophysical applications, rate coefficients determined by Elitzur and Watson (1978) by interpolation and extrapolation of the early calculations (Allison and Dalgarno 1967, Nishimura 1968) have been used.

It is now practical to carry out numerically exact calculations of the rotational excitation cross sections at low velocities which do not use the rigid rotor approximation and which include all the important reactive and non-reactive channels. We employ here the generalized Newton variational principle GNVP (Schwenke et al 1988, Sun et al. 1989) to calculate the cross

sections for the $j = 0 \rightarrow 1, 2, 3$ and $j = 1 \rightarrow 0, 2, 3$ transitions of H_2 in its lowest vibrational state with H at total energies below 0.9eV. We include all the contributing states, both open and closed, and obtain the non-reactive and reactive S matrix elements in the same calculation. The non-reactive calculations of Green and Truhlar (1979) were based on the LSTH potential energy surface (Truhlar and Horowitz 1978, 1979). We make use of the modified DMBE version (Varandas et al. 1987) which is designed to be more accurate at large separations of H and H_2 .

2 Theory

In the Arthurs-Dalgarno (1960) representation, the cross section for rotational transition of a diatom from rotational level j to rotational level j' by atom impact at a total energy E is given by

$$\sigma(E, j \rightarrow j') = \frac{\pi}{k_j^2} P(E, j \rightarrow j'), \quad (1)$$

where k_j is the wave number of the relative motion of the colliding particles and $P(E, j \rightarrow j')$ is given in terms of the S-matrix element S^J for the J^{th} partial wave by the expression

$$P(E, j \rightarrow j') = (2j + 1)^{-1} \sum_{J=0}^{J_{\text{max}}} (2J + 1) \sum_{l=|J-j|}^{J+j} \sum_{l'=|J-j'|}^{J+j'} |S^J(E, jl \rightarrow j'l')|^2, \quad (2)$$

The S-matrix for collisions of H and H₂ is given by

$$|S^J(E, jl \rightarrow j'l')|^2 = \begin{cases} |S_n^J(E, jl \rightarrow j'l') + S_r^J(E, jl \rightarrow j'l')|^2, & j, j' \text{ even;} \\ |S_n^J(E, jl \rightarrow j'l') - S_r^J(E, jl \rightarrow j'l')|^2 + & \\ + 2|S_n^J(E, jl \rightarrow j'l')|^2, & j, j' \text{ odd;} \\ 3|S_r^J(E, jl \rightarrow j'l')|^2, & j \text{ even, } j' \text{ odd;} \\ |S_r^J(E, jl \rightarrow j'l')|^2, & j \text{ odd, } j' \text{ even;} \end{cases} \quad (3)$$

where S_n^J and S_r^J are the non-reactive and reactive S-matrix elements respectively. Eq. (3) was obtained from formalism of Miller (1969) except that here we have reversed the sign of S_n^J in front of S_r^J to compensate for the geometric phase arising from the adiabatic separation of the electronic and nuclear motion (Mead and Truhlar 1979, Mead 1980, Lepetit and Kuppermann 1990). The permutation symmetry for three identical identical nuclei leads to an irreducible representation, which reduces the size of the problem to one third (Miller 1969, Schwenke et al 1989).

The rate coefficient is defined as

$$k(T, j \rightarrow j') = \frac{\hbar^2}{2\pi} \left(\frac{2\pi}{\mu k_B T} \right)^{\frac{3}{2}} \int_{E_0}^{\infty} dE \exp\left(-\frac{E - E_j}{k_B T}\right) P(E, j \rightarrow j'), \quad (4)$$

where k_B is Boltzmann's constant, T is the temperature, μ is the reduced mass of the colliding system, H-H₂, E_j is the rotational energy of level j of H₂, and E_0 is the larger value of E_j and $E_{j'}$.

3 Calculations

We calculated the S-matrix up to a total energy of 0.9eV, varying the basis function size to ensure numerical convergence to better than 5%. As the

energy increases, more partial-waves contribute, requiring more extensive calculations.

Reactive processes only occur at low values of the angular momentum J at which the projectile may overcome the centrifugal barrier and enter the short-range reaction region. At high J , the reactive channels may be neglected and the calculation simplifies to a non-reactive problem which requires much less computational effort. Near $E = 0.8\text{eV}$, for example, the reactive transition amplitudes become very small beyond $J = 15$ but the non-reactive ones do not until $J = 40$. According to Eq. (3), the integral cross section has more contributions from high J S-matrix elements due to the weighting factor $2J + 1$ and is less sensitive to the reactive processes that occur at low J . This is not true for differential cross sections where the low J contributions may dominate at particular scattering angles. In practice, we found also that below 1000K it is a valid approximation to neglect the closed ro-vibrational channels and the reactive channels for the para-para and ortho-ortho transitions.

Fig. I shows the calculated cross sections for the $j = 0 \rightarrow 1, 2, 3$ and $j = 1 \rightarrow 0, 2, 3$ transitions, from which we obtained rate coefficients with an error of less than 15%. We used cubic-spline fitting for the calculated $P(E)$, or $\log P(E)$ in the lower energy region, where $P(E)$ grows exponentially.

Table I lists the rate coefficients $k(j \rightarrow j')$ for the non-reactive rotational excitations $j = 0 \rightarrow 2$ and $j = 1 \rightarrow 3$. The rate coefficients of the inverse

transitions can be obtained according to

$$k(j' \rightarrow j) = \frac{2j+1}{2j'+1} \exp\left(\frac{E'_j - E_j}{k_B T}\right) k(j \rightarrow j') \times \begin{cases} 3 & j \text{ even and } j' \text{ odd,} \\ 1/3 & j \text{ odd and } j' \text{ even,} \\ 1 & \text{otherwise.} \end{cases} \quad (5)$$

The energies of the rotational levels of H_2 are $(E_j - E_0)/k_B = 170K, 509K$, and $1014K$ for $j = 1, 2, 3$ respectively.

The values for the $0 \rightarrow 2$ and $1 \rightarrow 3$ transitions are much larger than the rate coefficients calculated by Green and Truhlar (1979) which are also listed in Table I. Although the calculations of Green and Truhlar (1979) used the rigid rotor approximation and neglected closed channels and reactive channels, there seems little question that the large discrepancies arise primarily from the different potential energy surfaces employed in the two calculations. Given that they used a semi-classical method, the calculations of Mandy and Martin (1993), who also adopted the LSTH surface but did not use the rigid rotor approximation or neglect the reactive channels, are in acceptably close agreement with the results of Green and Truhlar (1979). Their values of $k(0 \rightarrow 2)$ and $k(1 \rightarrow 3)$ at 1000K are included in Table 1.

Further evidence is provided by unpublished preliminary semi-classical calculations by S. Lepp (private communication 1993) who obtains much larger values of $k(0 \rightarrow 2)$ and $k(1 \rightarrow 3)$ for the DMBE surface than for the LSTH surface.

The surfaces differ mostly in the long range region, to which the non-reactive cross sections are sensitive at low temperatures. It is claimed by

Varandas et al. (1987) that their potential is superior to the LSTH potential at large separations of H and H₂. If so, the rate coefficients we have presented in Table 1 are preferable to those of Green and Truhlar (1979) and Mandy and Martin (1993). By chance, they are of the same order of magnitude as the early calculations of Allison and Dalgarno (1967).

The rate coefficients may be conveniently represented as functions of temperature by the expressions

$$\begin{aligned} k(0 \rightarrow 2) &= \exp(-509/T) \times 10^{-13} \text{cm}^3 \text{s}^{-1} \begin{cases} (0.86T + 36), & 30K \geq T \leq 100K, \\ 1.3T, & 100K \geq T \leq 1000K, \end{cases} \\ k(1 \rightarrow 3) &= \exp(-844/T) \times 10^{-13} \text{cm}^3 \text{s}^{-1} \begin{cases} (0.29T + 5.9), & 30K \geq T \leq 100K, \\ (0.47T - 14), & 100K \geq T \leq 1000K, \end{cases} \end{aligned}$$

to within the accuracy of the calculated rate coefficients.

The rate coefficients for the reactive excitation and de-excitation processes are presented in Table 2. In contrast to the non-reactive excitation process, the values agree well at least at the common temperature of 1000K with the semi-classical results of Mandy and Martin (1993). At 1000K we obtain $k(0 \rightarrow 1) = 7.8 \times 10^{-13} \text{cm}^3 \text{s}^{-1}$, $k(0 \rightarrow 3) = 3.9 \times 10^{-13} \text{cm}^3 \text{s}^{-1}$ and $k(1 \rightarrow 2) = 2.1 \times 10^{-13} \text{cm}^3 \text{s}^{-1}$, whereas they calculated respectively $6.4 \times 10^{-13} \text{cm}^3 \text{s}^{-1}$, $4.7 \times 10^{-13} \text{cm}^3 \text{s}^{-1}$ and $1.9 \times 10^{-13} \text{cm}^3 \text{s}^{-1}$. The different potential energy surfaces used are quite similar at shorter distances of approach where reaction occurs. The agreement supports the utility of the semi-classical method above 600K (Mandy and Martin 1993). Takayanagi and

Masaki (1991) have used a simplified J_z -conserving coupled states method. With the LSTH surface they obtain $k(1 \rightarrow 0) = 1.9 \times 10^{-18} \text{cm}^3 \text{s}^{-1}$ and $4.4 \times 10^{-21} \text{cm}^3 \text{s}^{-1}$ at 200K and 100K, while we obtain $9.8 \times 10^{-19} \text{cm}^3 \text{s}^{-1}$ and $5.4 \times 10^{-22} \text{cm}^3 \text{s}^{-1}$. At low temperatures, the J_z conserving method is probably inadequate though some of the differences are due to the potentials. Experimental data are available for thermal rate coefficients between 300K and 444K. Schultz and LeRoy (1965) give an analytic fit to the data, reproduced in the review of Schofield (1967). We have complete results only for initially populated $j = 0$ and $j = 1$ levels so that no comparison is possible.

The uncertainties in the calculated rate coefficients may be as large as 15% at the lowest and largest temperatures. For the transitions from $j = 0$ to $j = 1, 3$ and $j = 1$ to $j = 2$, the analytical expressions:

$$k(0 \rightarrow 1) = \exp[(5.30 - 460/T)^2 - 21.2] 10^{-13} \text{cm}^3 \text{s}^{-1}, \quad (6)$$

$$k(0 \rightarrow 3) = \exp[(6.36 - 373/T)^2 - 34.5] 10^{-13} \text{cm}^3 \text{s}^{-1}, \quad (7)$$

$$k(1 \rightarrow 2) = \exp[(5.35 - 454/T)^2 - 23.1] 10^{-13} \text{cm}^3 \text{s}^{-1}. \quad (8)$$

provide fits to our results to within the accuracy of the calculated rate coefficients.

Acknowledgments

This work was supported by NASA grant NAGW-1561. It utilized the Cray-2 supercomputer of the National Center for Supercomputing Applications,

University of Illinois at Urbana-Champaign.

References

- Abgrall, H., Le Bourlot, J., Pineau des Forêts, Roueff, E., G., Flower, D.R. and Heck, L., 1992 *A&A* **253**, 525.
- Allison, A.C. and Dalgarno, A., 1967, *Proc. Phys. Soc. Lond.* **90**, 609.
- Arthurs, A. and Dalgarno, A., 1960, *Proc. Roy. Soc. Lond. A*, **256**, 540.
- Black, J.H., Dalgarno, A. and Weisheit, J.C., 1973, *Astrophys. Lett.* **14**, 77.
- Conrath, B.J. and Gierasch, P.J., 1984 *Icarus* **57**, 184.
- Chu, S.-I. and Dalgarno, A., 1990, *ApJ* **199**, 637.
- Dalgarno, A., Henry, R.J.W. and Roberts, C.S., 1966, *Proc. Phys. Soc.* **88**, 611.
- Dalgarno, A. and Black, J.H., 1977, *ApJS* **34**, 953.
- Elitzur, M. and Watson, W.D., 1978, *A&A* **70**, 443.
- Green, S. and Truhlar, D.G., 1979, *ApJ* **231**, L101.
- Kliner, D.A.V., Adelman, D.E. and Zare, R.N., 1991, *J. Chem. Phys.* **94**, 1069.

- Lepetit, B. and Kuppermann, A., 1990, *J. Chem. Phys.* **70**, 2284.
- Launay, J.M. and Le Dourneuf, M., 1989, *Chem. Phys. Lett.* **163**, 178.
- Mandy, M.E. and Martin, P.G., 1991, *J. Phys. Chem.* **95**, 8726.
- Mandy, M.E. and Martin, P.G., 1992, *J. Chem. Phys.* **97**, 265.
- Mandy, M.E. and Martin, P.G., 1993, *ApJS* **86**, 199.
- Manolopoulos, D.E. and Wyatt, R.E., 1989, *Chem. Phys. Lett.* **159**, 123;
- Manolopoulos, D.E. and Wyatt, R.E., 1990, *J. Chem. Phys.* **92**, 810.
- Massie, S.T. and Hunten, D.M., 1982, *Icarus* **49**, 213.
- McGuire, P. and Krüger, H., 1975, *J. Chem. Phys.* **63**, 6090.
- Mead C.A., 1980, *J. Chem. Phys.* **72**, 3839.
- Mead, C.A. and Truhlar, D.G., 1979, *J. Chem. Phys.* **70**, 2284.
- Miller, W.H., 1969, *J. Chem. Phys.* **50**, 407.
- Miller, W.H. and Zhang, J.Z.H., 1991, *J. Chem. Phys.* **95**, 12.
- Mladenovic, M., Zhao, M., Truhlar, D.G., Schwenke, D.W., Sun, Y. and Kouri, D.J., 1988, *J. Phys. Chem.* **92**, 7035.
- Nieh, J.-C. and Valentini, J.J., 1988, *Phys. Rev. Lett.* **60**, 519.

- Nieh, J.-C. and Valentini, J.J., 1990, *J. Chem. Phys.* **92**, 1083.
- Nishimura, S. 1968, *Ann. Tokyo Astr. Obs. 2nd ser.* **11**, 33.
- Park, T.J. and Light, J.C., 1989, *J. Chem. Phys.* **91**, 974.
- Pineau Des Forêts, G., Flower, D.R. and McCarroll, R., 1991, *MNRAS* **248**, 173.
- Schatz, G.C. and Kuppermann, A., 1976, *J. Chem. Phys.* **65**, 4668.
- Schwenke, D.W., K. Haug, M. Zhao, D.G. Truhlar, Y. Sun, Z.H.J. Zhang and D.J. Kouri, 1988, *J. Phys. Chem.* **92**, 3202.
- Schwenke, D.W., M. Mladenovic, M. Zhao, D.G. Truhlar, Y. Sun and D.J. Kouri, 1989, in *Supercomputer algorithms for reactivity, dynamics, and kinetics of small molecules*, ed. A. Lagana (Kluwer, Dordrecht) 131.
- Schofield, K., 1967, *Planet. Spa. Sci.* **15**, 643.
- Schultz, W.R. and LeRoy, D.J., 1965, *J. Chem. Phys.* **42**, 3869.
- Spitzer, L., Cochran, W.D. and Hirshfeld, A. 1974, *ApJS* **28**, 373.
- Sun, Y., C.-H. Yu, D.J. Kouri, D.W. Schwenke, P Halvick, M. Mladenovic and D.G. Truhlar, 1989 *J. Chem. Phys.* **91**, 1643.
- Takayanagi, K., Sakimoto, K. and Onda, K., 1987, *ApJ* **313**, L81.
- Takayanagi, K., Masaki, N., 1991, *J. Chem. Phys.* **95**, 4151.

- Truhlar, D.G. and C.J. Horowitz, 1978, *J. Chem. Phys.* **68**, 2466.
- Truhlar, D.G. and C.J. Horowitz, 1979, *J. Chem. Phys.* **71**, 1514.
- Varandas, A.J.C., Brown, F.B., Mead, C.A., Truhlar D.G. and Blais, N.G.
1987, *J. Chem. Phys.* **86**, 6258.
- Walker, F. and Light, J.C., 1989, *J. Chem. Phys.* **90**, 265 and 300.
- Wolken, G., Miller, W.H. and Karplus, M., 1972, *J. Chem. Phys.* **56**,
4930.
- Zhang, J.Z.H. and Miller, W.H., 1988, *Chem. Phys. Lett.* **153**, 465.
- Zhang, J.Z.H. and Miller, W.H., 1989, *Chem. Phys. Lett.* **159**, 130.

Figure captions

Fig.1: the cross sections for the transition from $j = 0$ to $j = 2$ and from $j = 1$ to $j = 3$.

Fig.2: the cross sections for the transition from $j = 0$ to $j = 1, 3$ and from $j = 1$ to $j = 2$.

Table 1. Rate coefficients for the $0 \rightarrow 2$ and $1 \rightarrow 3$ rotational excitation transition of H_2 by H impact*

T(K)	$0 \rightarrow 2$			$1 \rightarrow 3$		
	a	b	c	a	b	c
30	2.7(-19)			9.2(-25)		
40	2.1(-17)			1.2(-21)		
50	3.0(-16)			9.4(-20)		
60	1.8(-15)			1.8(-18)		
70	6.6(-15)			1.5(-17)		
80	1.8(-14)			7.5(-17)		
90	4.0(-14)			2.7(-16)		
100	7.7(-14)	1.0(-15)		7.7(-16)	7.5(-17)	
150	6.2(-13)			1.9(-14)		
200	1.9(-12)			1.1(-13)		
300	7.2(-12)	9.7(-14)		7.4(-13)	4.4(-14)	
400	1.5(-11)			2.1(-12)		
500	2.4(-11)	3.6(-13)		4.1(-12)	2.0(-13)	
600	3.4(-11)			6.7(-12)		
700	4.4(-11)			9.7(-12)		
800	5.4(-11)			1.3(-11)		
900	6.4(-11)			1.6(-11)		
1000	7.3(-11)	2.1(-12)	9.4(-12)	2.0(-11)	1.2(-12)	1.2(-12)

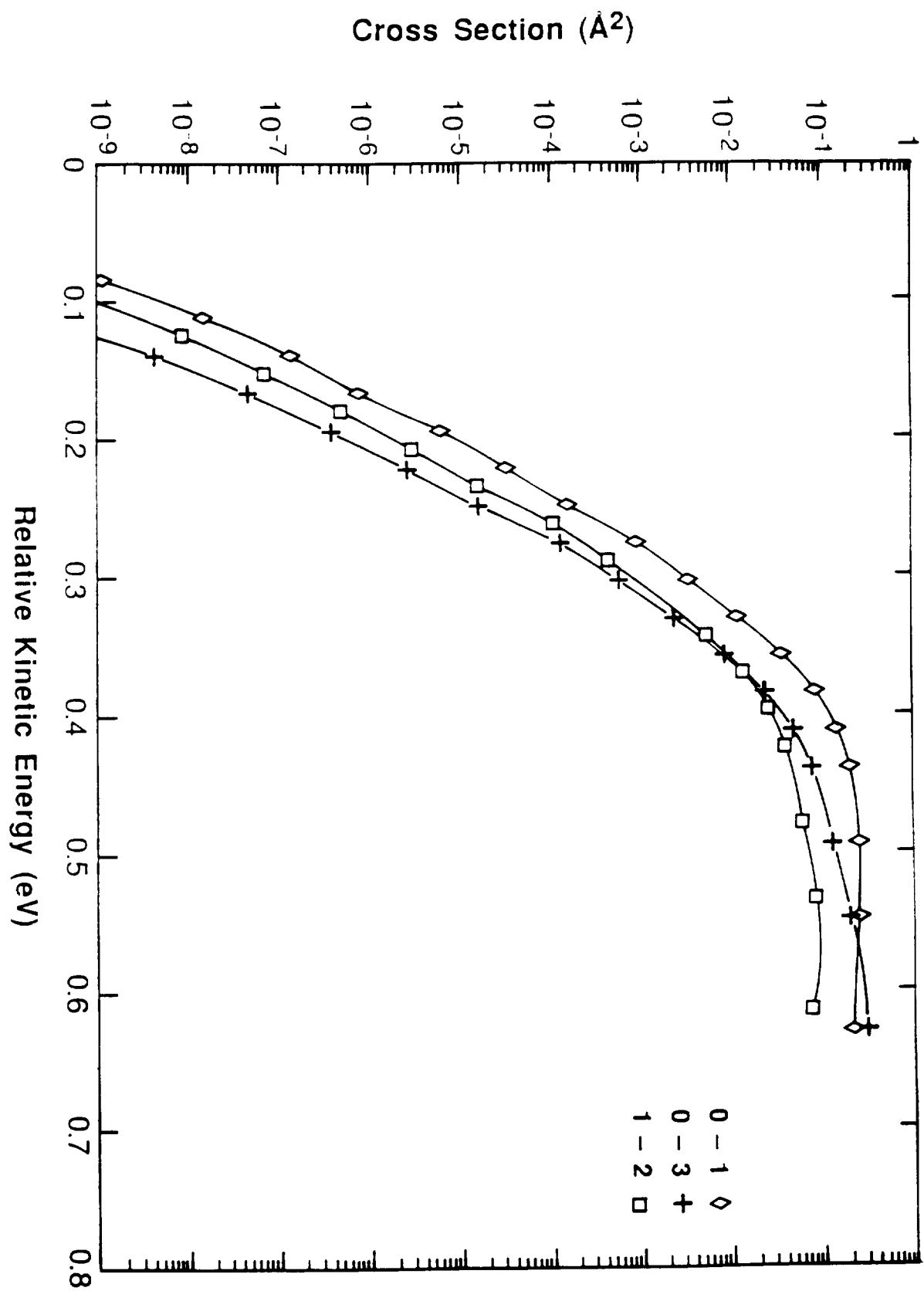
* in units of $cm^3 sec^{-1}$; number in parentheses is the power of 10;

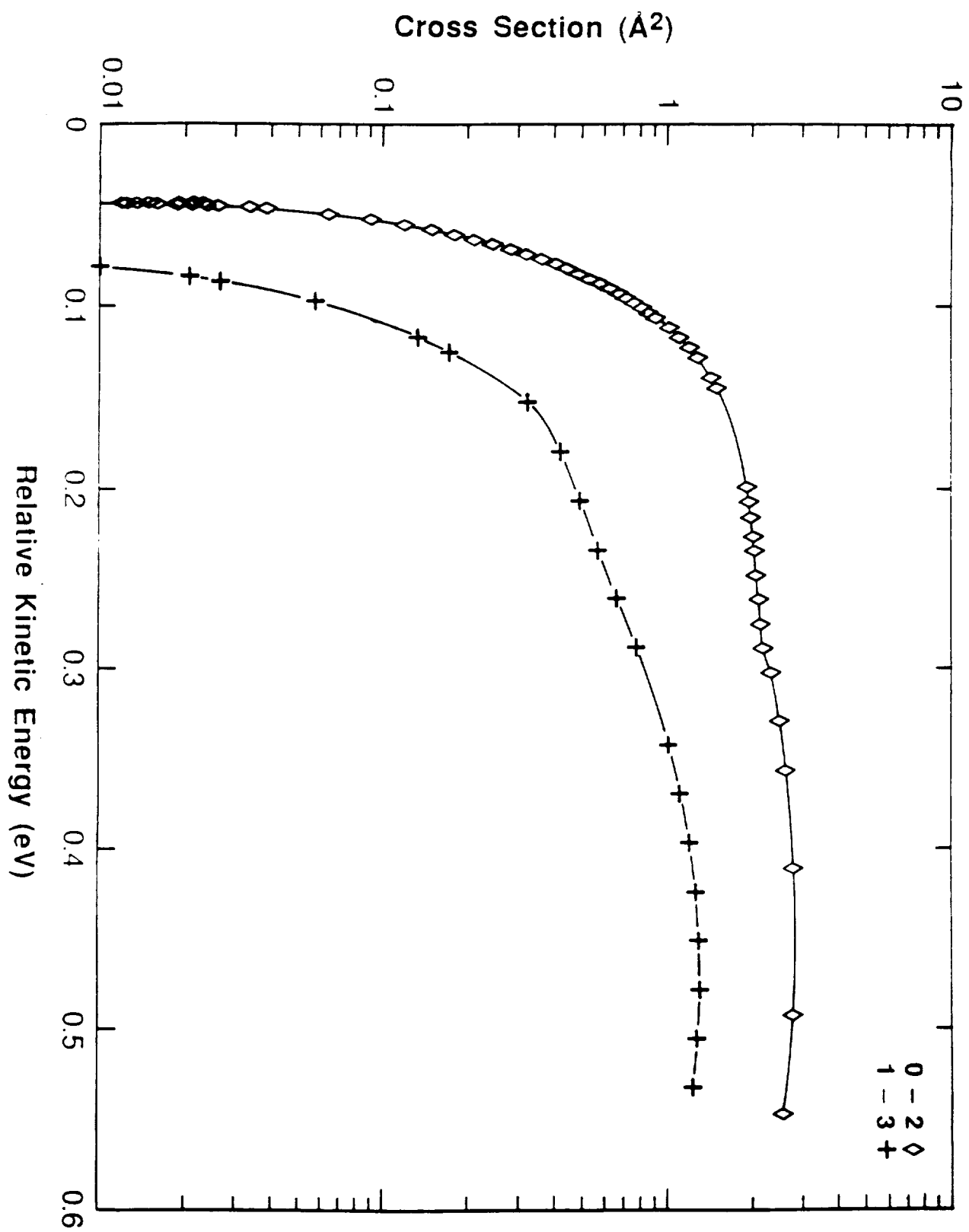
(a) this work, (b) Green and Truhlar (1979), (c) Mandy and Martin (1993).

Table 2. Rate coefficients for the $0 \rightarrow 1, 3$ and $1 \rightarrow 2$ rotational excitation transition of H_2 by H impact*

T(K)	$0 \rightarrow 1$	$0 \rightarrow 3$	$1 \rightarrow 2$
100	1.0 (-22)	1.0 (-24)	1.8 (-23)
150	8.5 (-21)	5.1 (-22)	1.9 (-21)
200	4.2 (-19)	5.7 (-20)	1.1 (-19)
300	9.3 (-17)	2.2 (-17)	2.3 (-17)
400	2.1 (-15)	6.1 (-16)	5.2 (-16)
500	1.5 (-14)	5.0 (-15)	3.7 (-15)
600	5.6 (-14)	2.1 (-14)	1.4 (-14)
700	1.4 (-13)	6.0 (-14)	3.7 (-14)
800	2.9 (-13)	1.3 (-13)	7.6 (-14)
900	5.1 (-13)	2.4 (-13)	1.3 (-13)
1000	7.8 (-13)	3.9 (-13)	2.1 (-13)

* in units of $\text{cm}^3\text{sec}^{-1}$; number in parentheses is the power of 10.







Harvard-Smithsonian Center for Astrophysics



Preprint Series

No. 3658
(Received June 15, 1993)

TERRESTRIAL AND EXTRATERRESTRIAL H_2^+

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To appear in
Advances in Atomic, Molecular and Optical Physics
(B. Bederson and H. Walther, editors)
Volume 32, 57, 1993

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1. Introduction

The molecular ion H_3^+ is the simplest stable polyatomic molecular system. It consists of two electrons and three protons. In the ground state, the protons occupy the vertices of an equilateral triangle. It is the major ion produced by high pressure electric discharges in hydrogen gas. Because of the simplicity of its structure, it has been a testing ground for theoretical methods of calculating potential energy surfaces and rotation-vibrational energy levels of polyatomic systems. The development of a quantitative picture of the structure of H_3^+ has occurred through a dynamic interplay of experimental and theoretical studies. These basic studies were crucial to the

identification of H_3^+ infrared emission in the spectra of the Jovian planets and must lead eventually to the detection of H_3^+ in absorption in the interstellar medium where it occupies a central role in interstellar chemistry. They have led to a tentative identification of H_3^+ in the envelope of supernova 1987a.

2. Terrestrial H_3^+

The early history of experiments on H_3^+ beginning with its discovery by J. J. Thomson (1911, 1912) has been described by Oka (1983, 1992). In the discharge the H_3^+ ions are produced by the conversion of the initial H_2^+ ions by the fast ion-molecule reaction



(Hogness and Lunn 1925, Stevenson and Schisler 1958, Varney 1960, Barnes, Martin and McDaniel 1961, Albritten, Miller, Martin and McDaniel 1968, Miller, Moseley, Martin and McDaniel 1968). Martin, McDaniel and Meeks (1961) and Secher and Williams (1969, 1970) pointed out that the same process operates in interstellar clouds so that H_3^+ will be present there to the near exclusion of H_2^+ . The reaction (1) is similarly effective in the ionospheres of the Jovian planets (Bauer 1973, Atreya, Donahue and McElroy 1974, Atreya 1986, Cravens 1987, McConnell and Majed 1987, Majed and McConnell 1991, Kim, Fox and Porter 1992). The laboratory studies on ion-mobilities in hydrogen (Albritten et al. 1968, Miller et al. 1968) also pointed to the three-body reactions



as additional sources of H_3^+ ions. The reaction of H^+ with vibrationally excited H_2 molecules in vibrational levels $v \geq 4$,



followed by reaction (1), may have contributed to the conversion of H^+ to H_3^+ . McElroy (1973)

suggested that reaction (4) plays a similar role in the Jovian atmospheres in addition to reactions (2) and (3) (Dalgarno 1972).

H_3^+ has been the subject of repeated quantum-mechanical calculations. Anderson (1992) has listed forty references to theoretical studies of the electronic potential energy surfaces published since the first analytic variational calculations of Hirschfelder (1938).

The availability of an accurate potential energy surface stimulated theoretical efforts to develop methods for the determination of the energy levels of complex molecules. Carney and Porter (1974, 1976) obtained a value of 2516 cm^{-1} for the frequency of the v_2 -fundamental band of H_3^+ which is within 5 cm^{-1} of the experimental value. Calculations with increasing accuracy have been presented since the studies of Carney and Porter, most recently by Spinko, Jensen, Bunker and Cejchan (1985), Tennyson and Sutcliffe (1986), Whinell and Light (1989), Tennyson and Henderson (1989), Bartlett and Howard (1990), Carter and Meyer (1990), Henderson, Miller and Tennyson (1990), Day and Trauhlar (1991), Henderson, Tennyson and Sutcliffe (1992), Carter and Meyer (1992) and Lie and Frye (1992). The frequency predicted by Lie and Frye is 2520.7 cm^{-1} which differs by -0.6 cm^{-1} from the experimental value of 2521.31 cm^{-1} . The discrepancy may be due to adiabatic corrections to the potential energy surface. There remain formidable difficulties in predicting accurately the positions of the high-lying rotation-vibration levels and in determining the density of states, but considerable progress has been made using quantum-mechanical (Henderson and Tennyson 1990, Bačić and Zhang 1991, 1992) and semi-classical methods (Berthinger, Schlier, Tennyson and Miller 1992). Accurate calculations of the partition function and equilibrium constant of reaction (1) have been carried out (Chandra, Gaur and Pande 1991, Sidhu, Miller and Tennyson 1992, Gaur, Pande and Chandra 1992).

The intense theoretical activity was stimulated by laboratory investigations. The infrared

absorption spectrum of H_3^+ was detected by Oka (1980) using a tunable laser infrared source and analyzed by J. K. G. Watson (cf. Oka 1992). Because of the large interaction between the rotational and vibrational motion, the identification of the spectral lines was far from obvious. There have been many subsequent investigations (cf. Oka 1992) and an extensive table of absorption lines has been presented by Kao, Oka, Miller and Tennyson (1991). Additional levels are given by Dinelli, Miller and Tennyson (1992). The measurements of absorption lines have been extended to the higher-lying bands (Bawendi, Rehfuss and Oka 1990, Xu, Gabrys and Oka 1990, Lee et al. 1991, Xu, Rösslein, Gabrys and Oka 1992).

Transition probabilities and line strengths have been presented by Pan and Oka (1986), Kao et al. (1991) and Dinelli et al. (1992).

Information about high-lying levels of H_3^+ near the dissociation limit has been obtained in a remarkable series of experiments by Carrington, Buttenshaw and Kennedy (1982), Carrington and Kennedy (1984) and Carrington and McNab (1989). They observed an infrared spectrum of H_3^+ between 872 cm^{-1} and 1094 cm^{-1} which contains nearly 27,000 lines. They measured the fragment H^+ ions and attributed the spectrum to transitions from discrete and quasi-bound rotation-vibrational levels of H_3^+ into predissociating levels which separate to $\text{H}^+ + \text{H}_2$.

The H_3^+ ion has also been seen in emission in the laboratory in the fundamental and overtone bands (Majewski et al. 1987, 1989) not long before its observation in the atmosphere of Jupiter.

3. Extraterrestrial H_3^+

3.1 The Jovian Planets

Emission lines of H_3^+ in the $2\nu_2(2) \rightarrow 0$ overtone band of H_3^+ are present in the spectrum of Jovian aurora taken by Traflet, Lester and Thompson (1989) on September 21, 1987,

although the identification of them was not made until later. They are present and correctly identified in the spectrum of Drossart et al. (1989). The history of the identification has been summarized by Oka (1992). The intensity distribution of Drossart et al. (1989) is consistent with an effective rotational temperature of $1100 \pm 100\text{ K}$ (Kim, Drossart, Caldwell and Maillard 1991). Oka and Geballe (1990) discovered the fundamental band of H_3^+ in the spectrum near 4μ and derived a rotational temperature of $670 \pm 100\text{ K}$. Maillard et al. (1990) also measured the emission lines of the fundamental band near 4μ and derived rotational temperatures of $1100 \pm 40\text{ K}$ and $835 \pm 50\text{ K}$ for the southern and northern zones respectively. Miller, Joseph and Tennyson (1991) measured the emission in the $2_11\mu$ and $4_0\mu$ regions in the overtone and fundamental bands and obtained a vibrational temperature of $1100 \pm 100\text{ K}$. Maillard et al. and Miller et al. noted that the level populations were close to thermal equilibrium at a temperature near 1000 K . Recently Drossart et al. (1992) have obtained a translational temperature of $1150 \pm 60\text{ K}$ from the widths of the H_3^+ lines.

The appearance of emission features over a broad range of infrared wavelengths at which imaging with an infrared camera can be carried out offers a marvelous opportunity for the observational study of auroral morphology in space and time (Kim et al. 1991, Baron et al. 1991, Drossart, Prangé and Maillard 1992, Billebaud et al. 1992).

Emission from H_3^+ has also been detected from Uranus (Traflet, Geballe and Miller 1992) and Saturn (Geballe, Jagod and Oka 1992).

The physics of the H_3^+ emission has been discussed in detail by Kim, Fox and Porter (1992). During the auroral bombardment, H_2^+ and H^+ ions are produced by the impact of energetic electrons. They are transformed into H_3^+ ions by reactions (1)-(4). The H_3^+ ions are removed by dissociative recombination



The process is critical to determinations of the abundance of H_3^+ in the Jovian atmospheres, in interstellar clouds and in the envelopes of supernovae.

The rate coefficient for dissociative recombination of H_3^+ has had an interesting history.

The earliest measurements (Lcu, Biondi and Johnsen 1973) of recombination in a stationary afterglow yielded a rate coefficient of $2.3 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ at 300K. Similar values were obtained in measurements using inclined beams (Pearl and Dolder 1974), merged beams (Auerbach et al. 1977, McGowan et al. 1979) and ion traps (Mahur, Khan and Hasled 1978). The rate coefficient was measured again in a pulsed afterglow over a wide range of temperatures and a rate coefficient varying between $1.6 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ at 240K and $1.2 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ at 50K was obtained (Macdonald, Biondi and Johnsen 1984). Then Adams, Smith and Alge (1984) employed a flowing afterglow Langmuir probe apparatus and were unable to detect dissociative recombination. They gave for the rate coefficient an upper limit at 300K of $2 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$, later reduced to $10^{-11} \text{ cm}^3 \text{ s}^{-1}$ (Adams and Smith 1987, 1988).

Their low value received support from theoretical calculations of the potential energy surfaces of H_3 (Kulander and Guest 1979, Michels and Hobbs 1984) which showed that none exists that would facilitate dissociative recombination of H_3^+ ions in the ground vibrational state. The discrepancy between the previous measurements and those of Adams, Smith and Alge was attributed to the presence of vibrationally excited H_3^+ or to contaminant ions like CH_5^+ (Johnsen 1987). A dependence on vibrational level population was found in merged beam experiments of Hus, Yousif, Sen and Mitchell (1988). However Amano (1988, 1990), exploiting the growing understanding of the absorption spectrum of H_3^+ , carried out an experiment using an infrared absorption technique, in which the recombination of H_3^+ ions in the $v=0$ level was measured. He

obtained a rate coefficient of $1.8 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ at 300K. The interpretation of his data was subject to some uncertainty because of possible contributions from collisional radiative recombination at high electron densities but the objections (Adams and Smith 1989) have been answered by Bates, Guest and Kendall (1993). New experiments using a modified flowing afterglow technique have been carried out by Canosa et al. (1992) who obtain large coefficients in agreement with the results of Amano (1988, 1990) and of earlier experimenters. Finally what seems to be overwhelming confirmation of a rate coefficient of the order of $10^{-7} (300T)^{1/2} \text{ cm}^3 \text{ s}^{-1}$ has come recently from merging beam cross section measurements using a storage ring (Larsson et al. 1993), the long lifetime of the mass-selected ions before recombination ensuring that only the $v=0$ level is populated.

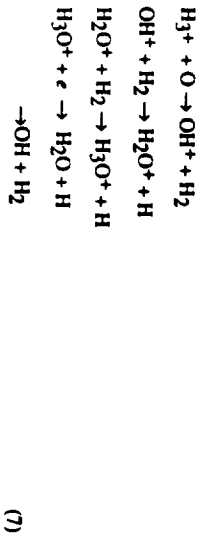
The basic question of the mechanism responsible for the rapid dissociative recombination remains to be answered. It does not proceed through a crossing of potentials. However Bates (1992) has suggested a mechanism in which curve crossing is not mandatory. In it the electron is captured into a Rydberg state, followed by a sequence of transitions into a higher-lying vibrational level of some Rydberg state from which predissociation to the repulsive potential of H_3 is effective. A more detailed model of Bates, Guest and Kendall (1993) offers some support for the mechanism, but the story is not yet over.

3.2 Jupiter Magnetosphere

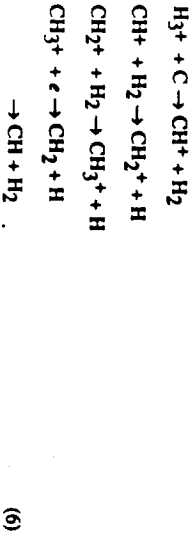
The first detection of extraterrestrial H_3^+ ions was not by observation of its electromagnetic spectrum but by discovery of an energetic mass 3 system in Jupiter's magnetosphere by the low energy particle telescope carried on Voyager 2 (Hamilton et al. 1980, 1981). The discovery was a clear indication of the presence of H_3^+ in the Jupiter ionosphere, providing a source for the magnetospheric ions. The mechanism that accelerates the ions presents a challenging problem in plasma physics.

3.3 Interstellar Space

The H_3^+ ion occupies a central place in the ion-molecule chemistry of interstellar clouds (Hechtst and Klemperer 1973). Following its production by cosmic ray ionization to produce H_2^+ and the conversion of H_2^+ to H_3^+ by reaction (1), H_3^+ may react with heavy atoms like oxygen and carbon to initiate reaction sequences such as



and



The laboratory data have enabled searches to be made for H_3^+ in interstellar clouds by looking for its absorption of radiation from infrared sources, but it has so far escaped detection (Oka 1981, Geballe and Oka 1989, Black, van Dishoeck, Willner and Woods 1990).

A measurement of its abundance would provide a measure of the cosmic ray ionizing flux in interstellar clouds. Thus if $\zeta \text{ s}^{-1}$ is the ionizing flux, the production rate of H_3^+ is $1.7 \zeta n(\text{H}_2) \text{ cm}^{-3} \text{ s}^{-1}$ where $n(\text{H}_2)$ is the number density of H_2 molecules and the additional 0.7 takes account of secondary ionization. The H_3^+ ions are removed by reactions with neutral constituents of the

gas, but mostly with O and CO,



We define an effective loss rate coefficient by

$$\bar{k} n(\text{H}_2) = \sum_i k_i n(x)$$

where $n(x)$ is the number density of constituent x and k_i is the rate coefficient for the reaction of H_3^+ with x . The H_3^+ ions are also removed by dissociative recombination (5) and (6) at a rate $\alpha n_e \text{ s}^{-1}$ where α is the rate coefficient for dissociative recombination. Then in equilibrium

$$n(\text{H}_3^+) = \zeta / (\bar{k} + \alpha n_e / n(\text{H}_2)) \tag{11}$$

Black et al. (1990) have shown how estimates may be made of the fractional electron density and the depletion of oxygen and carbon so that useful limits to ζ can be obtained from the upper limits to the H_3^+ column densities.

If H_2D^+ and H_3^+ were detected in the same location, the uncertainties in formula (11) could be removed. The deuterated ion H_2D^+ is produced by the reaction



and removed by the reverse reaction



and the analogs of (9) and (10)



and by dissociative recombination



If we adopt the same rate coefficients for H_2D^+ as for H_3^+ , we may write for the equilibrium

$$n(\text{H}_2\text{D}^+) = \frac{k_{12}n(\text{H}_3^+)n(\text{HD})}{k_{13}n(\text{H}_2) + \bar{k} n(\text{H}_2) + \alpha n_e}$$

where k_{12} and k_{13} are the rate coefficients of the corresponding reactions. Thus

$$\frac{n(\text{H}_2\text{D}^+)}{n(\text{H}_3^+)} = \frac{n(\text{HD})}{n(\text{H}_2)} f$$

where the factor f is an enhancement factor,

$$f = \frac{k_{12}}{k_{13} + \bar{k} + \alpha n_e/n(\text{H}_2)} ,$$

a result first given by Watson (1976). From it, we derive the relationship

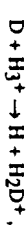
$$\bar{k} + \frac{\alpha n_e}{n(\text{H}_2)} = \frac{k_{12}}{f} \cdot k_{13}$$

so that expression (11) gives for ζ ,

$$\zeta = \left(\frac{k_{12}}{f} \cdot k_{13} \right) n(\text{H}_3^+) s^{-1} .$$

The rate coefficients k_{12} and k_{13} are known functions of the temperature (Smith, Adams and Alge 1982, Ikeda 1982, Sidhu, Miller and Tennyson 1992). The rate coefficient k_{13} for the endothermic reaction (1) becomes very slow at low temperatures and may be ignored in very cold clouds where the simple formula $\zeta = 4.12 n(\text{H}_3^+) V$ is applicable.

The chemistry must be modified to take into account the atom exchange reaction (Dalgarno and Lepp 1984)



because of the supply of deuterium atoms from the dissociative recombinations (16) and (18) of the enhanced H_2D^+ ions. A further source is



A tentative detection of H_2D^+ has been reported towards NGC 2264 (Phillips et al. 1985) but not confirmed (van Dishoeck, Phillips, Keene and Blake 1992, Pagani et al. 1992). An absorption feature towards the infrared source IRC2 in Orion has been found by Boreiko and Beitz (1993) and attributed by them to para H_2D^+ . Upper and lower limits to the fractional abundance of H_3^+ in several clouds have been estimated by van Dishoeck et al. (1992). It seems that the actual detection of interstellar H_3^+ cannot be long delayed.

3.4 Starburst galaxies

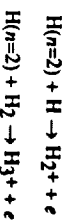
NGC 6240 is an ultraluminous infrared-bright galaxy, apparently undergoing a period of intense star formation. Very strong emission is seen from excited rotation-vibrational levels of H_2 . Draine and Woods (1990) have suggested the emission originates in molecular clouds subjected to transient X-radiation and have pointed out that absorption of the X-rays may lead to significant emission from the rotation-vibrational levels of H_3^+ . The X-rays heat the gas and ionize it. Their calculations assumed that dissociative recombination of H_3^+ is slow so that their calculated

intensities are overestimates. However they raise the intriguing possibility that H_3^+ emission may be a unique diagnostic of X-ray irradiated molecular gas.

3.5 Supernova 1987A

There are two strong unidentified emission features at 3.41 μm and 3.53 μm in the infrared spectrum of Supernova 1987A at day 192 after the explosion of a blue supergiant star in the Large Magellanic Cloud (Meikle et al. 1989). They can be matched by a thermal emission spectrum of H_3^+ at a temperature of about 1000-2000K (Miller, Tennyson, Lepp and Dalgarno 1992). No other convincing identification has yet been advanced.

The envelope chemistry is similar to that of the early Universe, supplemented by reactions



involving hydrogen atoms in the $n=2$ excited states. Reactions involving more highly excited states may also contribute to the formation of H_3^+ . The associative ionization of $H(2s)$ colliding with $H(1s)$ has been investigated experimentally and theoretically (Urban, Cornet, Brouillard and Giusti-Suzor 1991) and a value of the rate coefficient is available.

A detailed model of the chemistry of the envelope (Miller et al. 1992, Yan, Lepp and Dalgarno 1993) in which clumping has occurred appears to be successful in producing the inferred amount of H_3^+ at day 192 but the temperature of less than 2000K is lower than the model predicts.

Acknowledgments I am greatly indebted to the National Science Foundation, Division of Astronomical Sciences, and to the National Aeronautics and Space Administration for their support of my research. I am grateful to Drs. T. Oka and L. J. Lanzerotti for valuable criticisms of an earlier draft.

References

- Adams, N.G. and Smith, D. 1987 in *Astrochemistry IAU Symp.* 120 Ed. M.S. Vardya and S. P. Tarafdar (Reidel, Dordrecht) p. 1.
- Adams, N.G. and Smith, D. 1988 in *Rate coefficients in astrochemistry* (Kluwer, Dordrecht) p. 173.
- Adams, N.G., Smith, D. and Alge, E., 1984 *J. Chem. Phys.* **81**, 1778.
- Adams, N.G. and Smith, D. 1989 in *Dissociative recombination: Theory, Experiments and Applications*, Ed. J.B.A. Mitchell and S.L. Guberman (World Scientific, Singapore) p. 124.
- Albritton, D. L., Miller, T. M., Martin, D. W. and McDaniel, E. W. 1968 *Phys. Rev.* **171**, 94.
- Amano, T. 1988 *Astrophys. J.* **322**, L121.
- Amano, T. 1990 *J. Chem. Phys.* **92**, 6492.
- Anderson, J. B. 1992 *J. Chem. Phys.* **96**, 3702.
- Aureya, S. K. 1986 *Atmospheres and Ionospheres of the outer planets and their satellites* (Springer, New York).
- Aureya, S.K., Donahue, T.M. and McElroy, M.B. 1974 *Science* **184**, 154.
- Auerbach, D., Cacek, R., Candano, R., Gailly, T.D., Keyser, C.J., McGowan, J.W., Mul, P.M. and Wilk, S.F.J. 1977 *J. Phys. B* **10**, 3797.
- Bečič, Z. and Zhang, J. Z. H. 1991 *Chem. Phys. Lett.* **184**, 513.
- Bečič, Z. and Zhang, J. Z. H. 1992 *J. Chem. Phys.* **96**, 3707.
- Barnes, W.S., Martin D.W. and McDaniel, E.W. 1961 *Phys. Rev. Lett* **6**, 110.
- Baron, R., Joseph, R. D., Owen, T., Tennyson, J., Miller, S. and Ballesster, G. E. 1991 *Nature* **353**, 539.
- Bartlett, P. and Howard, B. J. 1990 *Mol. Phys.* **70**, 1001.
- Bates, D. R. 1992 *J. Phys. B.* **25**, 5479.
- Bates, D.R., Guest, M.F. and Kendall, R.A. 1993 *Planet Spa. Sci.* **44**, 9.

- Bauer, S. J. 1973 *Physics of planetary ionospheres* (Springer, New York).
- Bawendi, M. G., Rehruss, B. D. and Oka, T. 1990 *Chem. Phys.* **93**, 6200.
- Berthinger, M., Schlier, C., Tennyson, J. and Miller, S. 1992 *J. Chem. Phys.* **96**, 6842.
- Billebaud, F., Drossart, P., Maillard, J.-P., Caldwell, J. and Kim, S. 1992 *Icarus* **96**, 281.
- Black, J. H., van Dishoeck, E. F., Willner, S. P. and Woods, R. C. 1990 *Astrophys. J.* **358**, 459.
- Boreiko, R. T. and Betz, A. L. 1993 *Astrophys. J. Lett.* **405**, L39.
- Canosa, A., Gomet, J.C., Rowe, B.R., Mitchell, J.B.A., and Queffelec, J.L. 1992 *J. Chem. Phys.* **97**, 1028.
- Carney, G. D. and Porter, R. N. 1974 *J. Chem. Phys.* **60**, 4251.
- Carney, G. D. and Porter, R. N. 1976 *J. Chem. Phys.* **65**, 3547.
- Carrington, A. and Kennedy, R. A. 1984 *J. Chem. Phys.* **81**, 91.
- Carrington, A. and McNab, I.R. 1989 *Acc. Chem. Res.* **22**, 218.
- Carrington, A., Butenshaw, J. and Kennedy, R. A. 1982 *Mol. Phys.* **45**, 753.
- Carter, S. and Meyer, W. 1990 *J. Chem. Phys.* **93**, 8902.
- Carter, S. and Meyer, W. 1992 *J. Chem. Phys.* **96**, 2424.
- Chandra, S., Gaur, V.P. and Pande, M.C. 1991, *J. Quant. Spectr. Rad. Trans.* **45**, 57.
- Cravens, T. E. 1987 *J. Geophys. Res.* **92**, 11083.
- Dalgarno, A. 1972 *Applications in Astronomy in Phys. Electronic Atomic Collisions* (North Holland: Amsterdam) p. 381.
- Dalgarno, A. and Lepp, S. 1984 *Astrophys. J. Lett.* **287**, L47.
- Day, P. and Truhlar, D. G. 1991 *J. Chem. Phys.* **95**, 6615.
- Dinelli, B.M., Miller, S. and J. Tennyson 1992 *J. Mol. Spectr.* **153**, 718.
- Draine, B. T. and Woods, D. T. 1990 *Astrophys. J.* **363**, 464.
- Drossart, P., Maillard, J.-P., Caldwell, J., Kim, S. J., Watson, J.K.G., Majewski, W.A., Tennyson, J., Waite, J. H. and Wegener, R. 1989 *Nature* **340**, 539.

- Drossart, P., Maillard, J.-P., Caldwell, J. and J. Rosenqvist 1993 *Astrophys. J. Lett.* **402**, L25.
- Drossart, P., Prangé, R. and Maillard, J.-P. 1992 *Icarus* **92**, 10.
- Gaur, V.P., Pande, M.C. and Chandra, S. 1992 *Astrophys. Spa. Sci.* **191**, 147.
- Geballe, T. R., and Oka, T. 1989 *Astrophys. J.* **342**, 855.
- Geballe, T. R., Jagod, M.-F. and Oka, T. 1993 *Astrophys. J. Lett.* **408**, L109.
- Hamilton, D. C., Gloeckler, G., Krimigis and Lanzetta, L.J. 1981 *J. Geophys. Res.* **86**, 8301.
- Hamilton, D. C., Gloeckler, G., Krimigis, S. M., Bostrom, C. O., Armstrong, T. P., Axford, W.I., Fan, C.Y., Lanzetta, L.J. and Hunten, D.M. 1980 *Geophys. Res. Lett.* **7**, 813.
- Henderson, J. R. and Tennyson, J. 1990 *Chem. Phys. Lett.* **173**, 133.
- Henderson, J. R., Miller, S. and Tennyson, J. 1990 *J. Chem. Soc. Faraday Trans. 86*, 1963.
- Henderson, J. R., Tennyson, J. and Sutcliffe, B. T. 1992 *J. Chem. Phys.* **96**, 2426.
- Hierbst, E. 1982 *Astron Astrophys.* **111**, 76.
- Hierbst, E. and Klempner, W. 1973 *Astrophys. J.* **185**, 505.
- Hirschfelder, J. O. 1938 *J. Chem. Phys.* **6**, 795.
- Hogness, T. R. and Lunn, E. G. 1925 *Phys. Rev.* **26**, 44.
- Hus, H., Yousif, F.B., Sen, A. and Mitchell, J.B.A. 1988 *Phys. Rev. A* **38**, 658.
- Johnsen, R. 1987 *Int. J. Mass Spectr. Ion Proc.* **81**, 67.
- Kao, L., Oka, T., Miller, S. and Tennyson, J. 1991 *Astrophys. J. Suppl.* **77**, 317.
- Kim, S. J., Drossart, P., Caldwell, J., Maillard, J.-P. 1990 *Icarus* **84**, 54.
- Kim, S. J., Drossart, P., Caldwell, J., Maillard, J.-P., Herbst, E. and Shure, M. 1991 *Nature* **353**, 635.
- Kim, Y. H. and Fox, J. L. 1991 *Geophys. Res. Lett.* **18**, 123.
- Kim, Y. H., Fox, J. L. and Porter, H. S. 1992 *J. Geophys. Res.* **97**, 6093.

- Kulander, K.C. and Guest, F. 1979 *J. Phys. B*, **12**, L501.
- Larson, M., Danared, H., Mowat, J. R., Sigraay, P., Sundström, G., Borström, L., Filevich, A., Kallberg, A., Mannertik, S., Rensfelt, K. G. and Datz, S. 1993 *Phys. Rev. Lett.* **70**, 430.
- Lee, S.S., Venturdo, B.F., Cassidy, D.T., Oka, T., Miller, S. and Tennyson, J. 1991 *J. Mol. Spectr.* **145**, 222.
- Leu, M. T., Biondi, M. A. and Johnsen, R. 1973 *Phys. Rev. A*, **8**, 413.
- Lie, G. C. and Fyfe, D. 1992 *J. Chem. Phys.* **96**, 6784.
- Macdonald, J. A., Biondi, M. A. and Johnsen, R. 1984 *Planet. Spa. Sci.* **32**, 651.
- Maillard, M.-P., Drossart, P., Watson, J.K.G., Kim, S.J. and Caldwell, J. 1990 *Astrophys. J. Lett.* **363**, L37.
- Majeed, T. and McConnell, J. C. 1991 *Planet. Spa. Sci.* **39**, 1715.
- Majewski, W. A., Marshall, M. D., McKellar, A.R.W., Johns, J.W.C. and Watson, J.K.G. 1987 *J. Mol. Spectr.* **122**, 341.
- Majewski, W. A., Feldman, P.A., Watson, J.K.G., Miller, S. and Tennyson, J. 1989 *Astrophys. J. Lett.* **347**, L51.
- Martin, D. W., McDaniel, E. W. and Meeks, M. L. 1961 *Astrophys. J.* **134**, 1012.
- Mathur, D., Khan, S.U. and Hasted, J.B. 1978 *J. Phys. B*, **11**, 3615.
- McConnell, J. C. and Majeed, T. 1987 *J. Geophys. Res.* **92**, 8570.
- McElroy, M.B. 1973 *Spa. Sci. Rev.* **14**, 460.
- McGowan, J.W., Mul, P.M. D'Angelo, V.S., Mitchell, J.B.A., DeFrance, P. and Froelich, H.R. 1979 *Phys. Rev. Lett.* **42**, 373.
- Meikle, W.P.S., Allen, D.A., Spyromilio, J. and Varani, G.F. 1989 *Mon. Not. Roy. Astron. Soc.* **238**, 193.
- Michels, H.H. and Hobbs, R.H. 1984 *Astrophys. J. Lett.* **286**, 627.
- Miller, S. and Tennyson, J. 1989 *J. Mol. Spectr.* **136**, 223.
- Miller, S., Joseph, R. D. and Tennyson, J. 1990 *Astrophys. J. Lett.* **360**, L55.

- Miller, S., Tennyson, J., Lepp, S. and Dalgarno, A. 1992 *Nature* **355**, 420.
- Miller, T. M., Mosely, J. T., Martin, D. W. and McDaniel, E. W. 1968 *Phys. Rev.* **173**, 115.
- Oka, T. 1980 *Phys. Rev. Lett.* **45**, 531.
- Oka, T. 1981 *Phil. Trans. Roy. Soc. Lond. A* **303**, 543.
- Oka, T. 1983 in *Molecular Ions: Spectroscopy, Structure and Chemistry*, ed. T. A. Miller and V. E. Bondybey (North Holland) p. 73.
- Oka, T. 1992 *Rev. Mod. Phys.* **64**, 1141.
- Oka, T. and Geballe, T. R. 1990 *Astrophys. J.* **351**, L53.
- Paganí, L., Wannier, P. G., Freckling, M. A. et al. 1992 *Astron. Astrophys.* **258**, 472.
- Pan, F.S. and Oka, T., 1986 *Astrophys. J.* **305**, 518.
- Pear, B. and Dolder, K.T., 1974 *J. Phys. B* **7**, 1567 and 1948.
- Phillips, T. G., Blake, G. A., Keene, J. Woods, R. C. and Churchwell, E. B. 1985 *Astrophys. J. Lett.* **294**, L45.
- Sidhu, K.S., Miller, S. and Tennyson, J. 1992 *Astron. Astrophys.* **255**, 453.
- Smith, D., Adams, N. G. and Alge, E. 1982 *Astrophys. J.* **263**, 123.
- Spitko, V., Jensen, P., Bunker, P.R. and Cepchan, A. 1985 *J. Mol. Spectr.* **112**, 183.
- Stecher, T. P. and Williams, D. A. 1969 *Astrophys. Lett.* **4**, 99.
- Stecher, T. P. and Williams, D.A. 1970 *Astrophys. Lett.* **7**, 59.
- Svensson, D. P. and Schissler, D. O. 1958 *J. Chem. Phys.* **29**, 282.
- Tennyson, J. and Henderson, J. R. 1989 *J. Chem. Phys.* **91**, 3815.
- Tennyson, J. and Sutcliffe, B. T. 1986 *Mol. Phys.* **58**, 1067.
- Thomson, J. J. 1911, *Phil. Mag.* **21**, 225.
- Thomson, J. J. 1912 *Phil. Mag.* **24**, 209.
- Trafton, L., Geballe, T. R., Miller, S., Tennyson, J. and Ballester, G. E. 1993 *Astrophys. J.* **405**, 761.
- Trafton, L., Lester, D. F. and Thomson, K.L. 1989 *Astrophys. J. Lett.* **343**, L73.

- Urbain, X., Comet, A., Brouillard, F. and Giusti-Suzor, A. 1991 *Phys. Rev. Lett.* **66**, 1685.
- van Dishoeck, E. F., Phillips, T. G., Keene J. and Blake, G. A. 1992 *Astron. Astrophys* **261**, L13.
- Varney, R. N. 1960 *Phys. Rev. Lett.* **5**, 559.
- W. D. Watson 1976 *Rev. Mod. Phys.* **48**, 513.
- Whitnell, R. M. and Light, J. C. 1989 *J. Chem. Phys.* **90**, 1774.
- Xu, L.-W., Gabrys, C.M. and Oka, T. 1990 *J. Chem. Phys.* **93**, 6210.
- Xu, L.-W., Rüsselein, M., Gabrys, C.M. and Oka, T. 1992 *J. Mol. Spectr.* **153**, 726.
- Yan, M., Lepp, S. and Dalgarno, A. 1993 (in preparation).

